



Electronic structure of heterojunction $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalyst for oxidative desulfurization

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ABSTRACT

Electronic structure of active sites plays a crucial role in redox catalysts. Herein, graphitic carbon nitride (g- C_3N_4) decorated with metallic MoO_2 heterojunction nanocomposites were successfully synthesized through a facile calcination route. XPS, UPS, UV–vis and PL spectra results suggest electron transfer from the conduction band (CB) of g- C_3N_4 to unfilled π^* band of metallic MoO_2 in the metal-semiconductor heterojunction. The electron transfer ensures high intrinsic oxidative desulfurization activity for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites. Radical scavenger experiments indicate that the electron transfer facilitates the enrichment of electron density around Mo active sites and control the rate-determining step of oxidative desulfurization. The approach can be extended to other low valent transition metal oxides possessing *d* electrons for enhanced catalytic activity in redox reactions.

1. Introduction

Sulfur contents in fuel oils have been restricted to ultra-low level (< 10 ppm) in many countries due to stringent environmental regulations [1]. The conventional hydrosulfurization (HDS) process is widely applied to remove organosulfur compounds in petroleum hydrofining industry [2]. However, HDS is limited to eliminate refractory substituted dibenzothiophenes such as 4, 6-DMDBT (owing to steric hindrance) from oils. Oxidative desulfurization (ODS) has been regarded as a prospective and green technology for ultra-deep desulfurization due to its mild reaction conditions (room temperature and atmospheric pressure) and high efficiency. It is reported that highly substituted dibenzothiophenes can be most readily oxidized compared with thiophene by ODS reaction. [3,4].

In the past decade, many scientific research workers were looking forward to seeking a catalyst with an excellent performance on oxidation desulfurization. Several catalysts, such as metal oxides [3,5] or metal-based ionic liquid-supported catalysts [4,6], zeolites [7], metal-organic framework (MOF)-supported catalysts [8], and poly-oxometalates [9], have been used to eliminate sulfur species from fuel oil. Among them, transition metal-based (Mo, W, Ti, V, etc.) materials are promising for the ultra-deep desulfurization of fuel oil under mild

conditions [10–12]. In particular, MoO_3 heterogeneous catalysts are reported to be remarkably successful for the ODS process. Many kinds of supports, such as titania, alumina, mesoporous silica, activated carbons and so on, have been generally used for preparation of supported MoO_3 catalysts. For example, Kabe and coauthors reported MoO_3 catalysts supported on Al_2O_3 exhibit high activity in ODS with TBHP as oxidant [6]. Wang et al. investigated P-modified $\text{MoO}_3/\text{SiO}_2$ catalysts with significant ODS performance [13]. $\text{MoO}_x\text{-VO}_x/\text{Al}_2\text{O}_3$ and $\text{MoO}_x\text{-VO}_x$ catalysts were synthesized for oxidative desulfurization and obtained desulfurization rate of 97% for DBT under the optimum reaction conditions [14]. We also reported that mesoporous SiM41C supported MoO_3 catalysts, which successfully reduced S content in a model fuel from 500 ppm to 0 ppm by ODS using TBHP as the oxidant [15]. To date, although many supports have been illustrated to be good for ODS, it is still a challenge to look for a new interesting support with high performance. Another extremely important point is the absence of systematic studies on the relationship between the catalytic efficiency and the catalyst structure, especially, the synergetic effect between the active sites and the supports. Rodriguez-Gattorno et al. investigated the origin of the acidity related to catalytic efficiency for $\text{WO}_x\text{-ZrO}_2$ catalyst and found that the increase of Brönsted acidity density favored ODS activity [11]. Zhang et al. indicate that the oxidizability of tungstate

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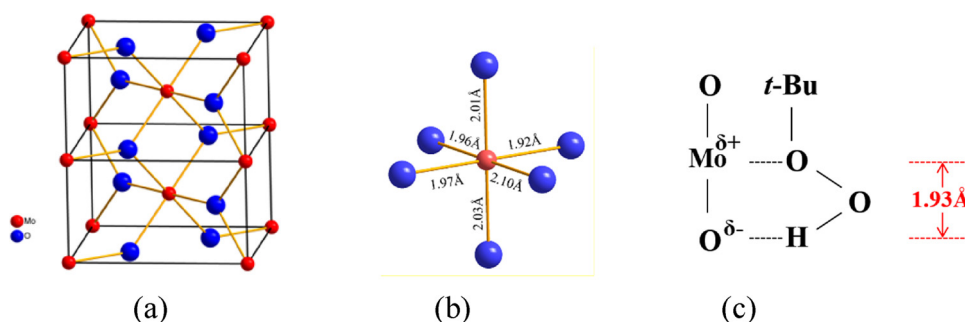
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Scheme 1. (a) distorted rutile structure of MoO_2 . (b) bond lengths of distorted MoO_6 octahedron in MoO_2 . (c) the coordination of TBHP to Mo-O bond on MoO_2 .

plays a synergistic role in activation of reactants and results in excellent ODS performance [4]. However, there are few studies focused on the electronic structures of ODS catalysts.

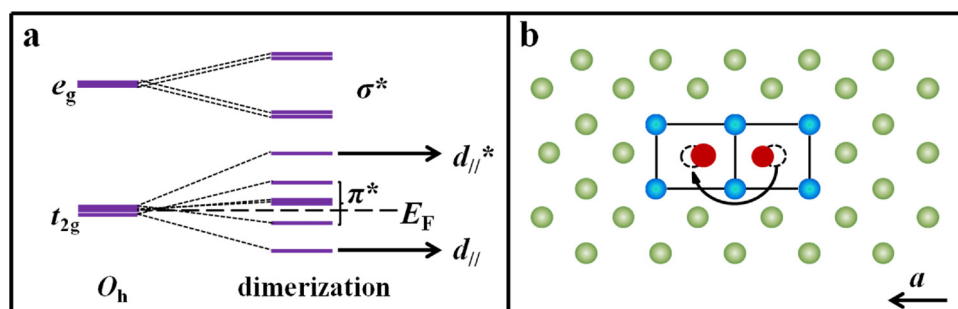
In our previous study [6,15], MoO_3 catalyst presents high performance in ODS reaction with *tert*-butyl hydroperoxide (TBHP) as the oxidant and Mo-O bond acts as the active site. Mo-O bond lengths of MoO_6 distorted octahedron in MoO_3 orthorhombic crystal structure are 1.67, 1.73, 1.94, 1.94, 2.25, 2.33 Å [16]. Lower valent MoO_2 can be easily obtained by the reduction of MoO_3 . The monoclinic structure (P21/c) for MoO_2 crystal ($a = 5.61$, $b = 4.86$, $c = 5.63$ Å, $\beta = 121^\circ$, $Z = 4$) is shown in Scheme 1a. In this distorted rutile structure with MoO_6 distorted octahedron, two distinct Mo-Mo metal to metal bonds (2.51 and 3.10 Å) are formed, which causes two distinguishing oxygen coordination circumstances: (i) with Mo-O bond lengths of 1.92, 2.01 and 1.96 Å, (ii) with slightly longer Mo-O bond lengths of 1.97, 2.03 and 2.10 Å (Scheme 1b) [17]. Compared with MoO_3 , MoO_2 shows appropriate Mo-O bond lengths for ODS reaction (Scheme 1c). The distance between the hydrogen atom and the peroxy oxygen atom neighboring to *tert*-butyl group is 1.93 Å, the coordination of peroxy O—O—H bonds to Mo-O bond on MoO_2 constructs a five-member ring more easily than that on MoO_3 , which is expected to enhance the oxidizability of the peroxy oxygen atom.

MoO_2 is less studied than MoO_3 . Formally MoO_2 is a $4d^2$ Mo (IV) compound, which exhibits a metallic behavior [18]. The interpretation is that the Fermi level E_F of MoO_2 is located within Mo_{4d} orbitals [19]. Usually, d orbitals of transition metal oxides separate into t_{2g} and e_g orbitals due to crystal field effect in octahedral (O_h) symmetry. However, as shown in Scheme 2a, the x^2-y^2 (t_{2g}) orbital for MoO_2 is divided into bonding ($d_{//}$) and antibonding bands ($d_{//}^*$) in virtue of paired Mo ions along monoclinic a axis (Scheme 2b). Other t_{2g} (xz, yz) orbitals and e_g (z^2, xy) orbitals show less influence by Mo dimerization (labeled as π^* and σ^* bands, respectively) [20]. As to the Fermi level E_F of MoO_2 , according to ultraviolet photoelectron spectroscopy (UPS) measurements and density-functional-theory (DFT) calculations, two Mo_{4d} bands just lie below the Fermi level: at ~ 0.5 and ~ 1.5 eV in experiment and at ~ 0.3 and ~ 1.5 eV in theory [17,21,22]. $d_{//}$ band below Fermi level is fully occupied. π^* band around Fermi level can hold four

electrons per Mo^{4+} cation. However, only one extra electron per Mo^{4+} cation is possessed in the lowest energy band of π^* band, the π^* band around Fermi level is less than half-full. As a result MoO_2 presents metallic conductivity by metal-metal bonding. The Mo_{4d} bands around Fermi level will take part in redox processes.

Recently, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) attracts many interests for its good photocatalytic activity and moderate band gap energy (E_g) as a semiconductor [23]. $\text{g-C}_3\text{N}_4$ shows two-dimensional structure with N-bridged tri-s-triazine repeating units [24]. DFT calculations indicate the band gap in the melem molecule is 2.67 eV, which is supported by the ultraviolet-visible experiments [25,26]. The valence band (VB) for the melem molecule is a combination of the highest occupied molecular orbital (HOMO) levels, which are donated by nitrogen p_z orbitals. The conduction band (CB) for the melem molecule can be related to the lowest unoccupied molecular orbital (LUMO) levels, which mainly consist of carbon p_z orbitals [23]. Carbon atom in the melem molecule presents sp^2 hybridization, and each carbon atom possesses one free electron in carbon p_z orbitals. Recent studies show that coating MoO_3 with $\text{g-C}_3\text{N}_4$ decreases the electron-hole recombination and obtains enhanced efficiency of photocatalysts [27–29]. However, there are relatively few studies devoted to low valent $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalyst.

As expected, MoO_2 shows appropriate Mo-O bond lengths for ODS reaction, the electrons in Mo_{4d} bands around Fermi level will have an effect on redox processes. Moreover, the electrons in carbon p_z orbitals of $\text{g-C}_3\text{N}_4$ will also play some important roles due to the combination of metallic MoO_2 and semiconducting $\text{g-C}_3\text{N}_4$. In this work, a facile route to synthesize a series of $\text{MoO}_2/\text{g-C}_3\text{N}_4$ metal-semiconductor heterojunction composites is developed and such heterojunction composites show remarkably enhanced ODS activity. Owing to that the electronic structure of $\text{MoO}_2/\text{g-C}_3\text{N}_4$ is very important and has not yet been understood, the nature of synergic effect between MoO_2 and $\text{g-C}_3\text{N}_4$ is clearly elucidated and the ODS mechanism is further discussed in this paper.



Scheme 2. (a) crystal field effect on Mo_{4d} levels for Mo-Mo dimerization. (b) Mo-Mo bonding along monoclinic a axis, red and blue circles represent molybdenum and oxygen ions [20].

2. Experimental

2.1. Catalyst preparation

According to the previous research [30], the bulk g-C₃N₄ powders were prepared by calcination of melamine. 10 g melamine was placed in a 50 ml crucible with cover, then heated by a rate of 3 °C/min using muffle furnace and kept for 2 h at 550 °C. Yellow products were obtained and then milled for 15 min.

MoO₂/g-C₃N₄ catalyst was synthesized by impregnation method together with ultrasonic-assisted dispersion. A certain amount of g-C₃N₄ powder and calculated amount of (NH₄)₆Mo₇O₂₄·4H₂O (equal to 20 wt % MoO₂) were added into 60 ml distilled water under stirring for 1 h, followed by ultrasonic agitation for 0.5 h, then dried with rotary evaporation at 70 °C. The obtained precursor powder was ground and placed in a quartz boat, then heated at different temperatures (450, 500, 550 and 600 °C) for 2 h with a rate of 5 °C/min under nitrogen atmosphere. The corresponding catalysts were marked as MoO₂/g-C₃N₄-x, where x means the calcination temperature under nitrogen atmosphere.

2.2. Catalyst characterization

X-ray diffraction (XRD) spectra of the catalysts were characterized by a Rigaku D/Max-2500 equipped with a Cu-target tube and scanned by a rate of 6.0°/min over the 2θ range of 10°–80°. Fourier transform infrared (FTIR) spectra were performed on a Bruker TENSOR 37. The morphology of the catalysts was examined by HRTEM and EDX (Philips Tecnai G2 F20 microscope). Thermogravimetric analysis (TG) is used to determine the real content of MoO₂ in the composites by a TA SDT Q600 instrument. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were operated on a Thermo Scientific ESCALAB 250Xi using excitation photon energy (1486.6 eV) for XPS and He I (*hν* = 21.22 eV) as the exciting source for UPS. Surface areas were calculated using N₂ adsorption/desorption BET method conducted at 77 K with a BELSORP-mini II sorption apparatus. The UV–vis diffused reflectance spectra (DRS) of the catalysts were carried out by a TU-1950 spectrophotometer. Photoluminescence spectra (PL) of the catalysts were tested on an F-7000 spectrometer, using a Xe lamp (350 nm) as light source.

2.3. Catalytic reaction

The as-prepared MoO₂/g-C₃N₄ catalysts were tested for oxidative desulfurization of DBT using a batch reactor. A simulated diesel oil (500 ppm DBT) was prepared as following: a solution of 500 mg/g of DBT was obtained by dissolving 0.05 g DBT in 99.95 g decalin. 0.1141 g *tert*-butyl hydroperoxide (TBHP) was then added in the DBT solution with the O/S molar ratio of 3.0 (moles of oxygen atom in TBHP/moles of sulfur atom in DBT). In a typical ODS procedure, 10 g simulated diesel oil in a 50 ml round bottom flask was heated to 80 °C under stirring, then 0.05 g catalyst was mixed and the ODS reaction lasted for 2 h. During the oxidation, the reaction products were detected every 10 min using a gas chromatograph (GC 2060) equipped with an FID.

2.3. Theoretical calculation methods

First-principles computations were performed through the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [31]. Projector augmented wave (PAW) based potentials were used to describe nuclei-electron interactions [32]. The Perdew-Burke-Ernzerhof form of the Generalized-Gradient Approximation was employed to describe electron exchange and correlation [33]. The wave functions at each k-point were expanded with a plane wave basis set and a kinetic cutoff energy up to 400 eV. The integration of the Brillouin zone was conducted using 2 × 3 × 1 Monkhorst-Pack

grids [34]. The electron occupancies were determined using Fermi broadening with a width of 0.1 eV. All geometries were fully relaxed and optimized until the energy was converged to 1.0 × 10^{−5} eV per atom and the force was converged to 0.05 eV/Å. DFT-D3 method with Becke-Jonson damping was applied to describe the van der Waals interactions [35,36]. The reaction pathways and energy barriers were calculated by the climbing-image nudged elastic band (CI-NEB) method [37]. The energy barrier (*E*) was defined as *E* = *E*_{TS} − *E*_{IS} and the reaction energy (Δ*E*) was calculated from the equation Δ*E* = *E*_{FS} − *E*_{IS}, where *E*_{IS}, *E*_{TS} and *E*_{FS} are the energy of the initial, transition and final state, respectively. According to this definition, the negative and positive values represent exothermic and endothermic reactions, respectively. The MoO₂ (011) surface was modeled with a 2 × 1 supercell, built from the optimized MoO₂ primitive cell. A vacuum space larger than 15 Å was inserted in the *z* direction to prevent interactions between periodically.

3. Results and discussion

3.1. Characterization of MoO₂/g-C₃N₄ catalysts

Fig. 1 shows XRD patterns of MoO₂/g-C₃N₄ catalysts calcined at different temperatures in nitrogen atmosphere. MoO₂/g-C₃N₄ composites can be obtained at 450, 500, 550 °C. The diffraction peaks of both g-C₃N₄ and MoO₂ can be observed in the obtained MoO₂/g-C₃N₄ composites, confirming the coexistence of g-C₃N₄ and MoO₂ [24,38]. It is obvious that the peak of g-C₃N₄ decreases with increasing calcination temperature up to 550 °C and disappears at 600 °C. Pure MoO₂ is obtained at 600 °C. These results can be interpreted with the decomposition of g-C₃N₄ at higher temperature. FTIR analysis (Fig. S1) further confirms that g-C₃N₄ maintains tri-s-triazine structure in the obtained MoO₂/g-C₃N₄ composites [39].

TG was carried out in air atmosphere to determine the real content of MoO₂ in as-synthesized MoO₂/g-C₃N₄ catalysts (Fig. 2). Pure g-C₃N₄ begins to decompose at temperature above 520 °C, while for MoO₂/g-C₃N₄ composites, the beginning of mass-loss shift to 420 °C. This result suggests that MoO₂ promotes the combustion of g-C₃N₄, which is confirmed by DSC results (Fig. S2), implying the synergic effect between MoO₂ and g-C₃N₄. Similar results are reported for MoO₃/g-C₃N₄, CeO₂/g-C₃N₄ and V₂O₅/g-C₃N₄ catalysts [29,40–42]. The gaining weight up to 350 °C for MoO₂/g-C₃N₄-600 (pure MoO₂) are matched well with the mass of MoO₂ oxidization to MoO₃, which is confirmed by XRD results. The real content of MoO₂ in MoO₂/g-C₃N₄ composites can be estimated

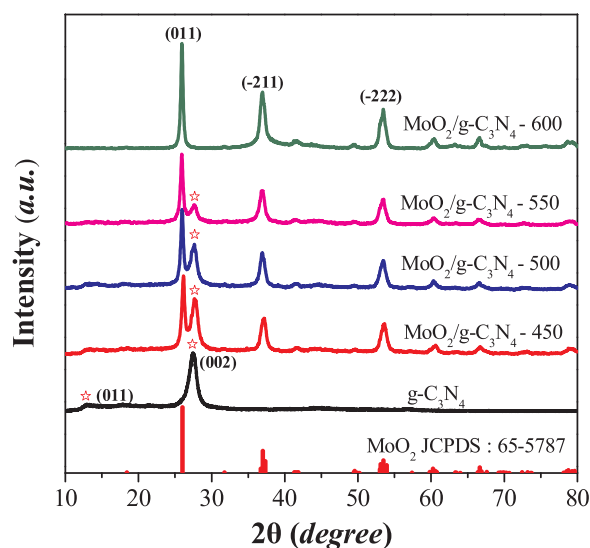


Fig. 1. XRD patterns of MoO₂/g-C₃N₄ catalysts obtained at different calcination temperatures (450, 500, 550 and 600 °C).

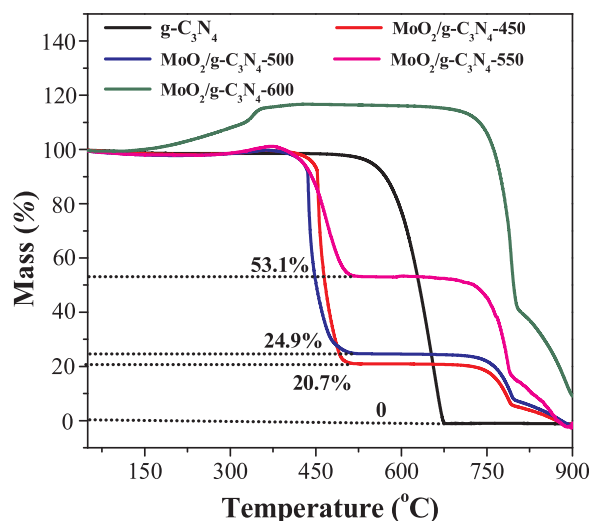


Fig. 2. TG curves in air atmosphere for as-synthesized MoO₂/g-C₃N₄ catalysts.

Table 1

Specific surface area, pore volume and MoO₂ content of as-synthesized catalysts.

Sample	Surface area (m ² /g)	Pore Volume (cm ³ /g)	MoO ₂ content per mass%
g-C ₃ N ₄	11	0.0834	0
MoO ₂ /g-C ₃ N ₄ - 450	40	0.2431	18.9
MoO ₂ /g-C ₃ N ₄ - 500	55	0.3432	22.7
MoO ₂ /g-C ₃ N ₄ - 550	77	0.5394	50.2
MoO ₂ /g-C ₃ N ₄ - 600	9	0.0997	100

from the remaining MoO₃ mass after heating above 600°C (Table 1). The weight loss above 750 °C is attributed to the sublimation of MoO₃ [29]. TG of the catalyst precursor was carried out in nitrogen atmosphere to determine the decomposition temperature during the catalyst preparation (Fig. S3). The results of XRD, FTIR and TG indicate that MoO₂/g-C₃N₄ composites with different MoO₂ content (19–50 wt%) have been successfully synthesized.

The nitrogen adsorption-desorption curves of the catalysts are displayed in Fig. S4. The BET surface areas of synthesized MoO₂/g-C₃N₄ catalysts are listed in Table 1. With an increase in the calcination temperature up to 550 °C, both surface area and pore volume of the catalysts increase, and MoO₂ loading also increases. MoO₂/g-C₃N₄-600 shows lowest surface area and pore volume which is attributed to the formation of pure bulk MoO₂ (g-C₃N₄ decomposed completely).

The morphological features of pure g-C₃N₄ and MoO₂/g-C₃N₄ composites were examined by TEM. Pure g-C₃N₄ (Fig. 3a) appears to be a lamellar structure, which the monolayer surface is very smooth. With increasing Mo contents in MoO₂/g-C₃N₄-450, -500 and -550 samples (Fig. 3b-d), some monolayer-dispersed MoO₂ clusters together in bulk MoO₂. Despite high MoO₂ content (50 wt%) in MoO₂/g-C₃N₄-550 sample, most of MoO₂ are well-dispersed on the lamellas of g-C₃N₄ nanosheets except for some bulk MoO₂ marked by red ring in Fig. 3d. A clear lattice fringe of 0.3447 nm is observed for the bulk MoO₂ by HRTEM image in Fig. 3e, which is consistent with the interplanar spacing of (011) plane (JCPDS 65–5787, $d_{011} = 0.3423$ nm) [38]. It is demonstrated that MoO₂/g-C₃N₄ composites are formed by the coupling of MoO₂ {011} crystal planes and g-C₃N₄ sheets. MoO₂/g-C₃N₄-600 sample (Fig. 3f) presents to be pure MoO₂ according to the interplanar spacing of the clusters. EDX spectrum (Fig. 3g) confirms that MoO₂/g-C₃N₄-550 sample includes C, N, Mo and O elements. Elemental mapping analyses (Fig. 3h-m) of N element (green) and Mo element (red) for MoO₂/g-C₃N₄ composites give the results that MoO₂ is well-dispersed on g-C₃N₄ nanosheets. Further, with increasing Mo contents

in MoO₂/g-C₃N₄ composites the dispersion degree of MoO₂ decreases. Based on the above results, the well dispersed MoO₂ enables more intimate contact with g-C₃N₄ for synergetic effect compared with the bulk MoO₂ as shown in Scheme 3. MoO₂/g-C₃N₄-450 sample is suggested to allow highly dispersed MoO₂ on g-C₃N₄ due to its low Mo loading and low calcination temperature compared with MoO₂/g-C₃N₄-500 and -550 samples.

XPS analysis was performed to determine the surface electronic structure of MoO₂/g-C₃N₄ catalysts calcined at different temperatures. XPS spectra are shown in Fig. 4 and peak fitting results are shown in Fig. S5. From Fig. 4a, at the binding energies of 284.8 and 288.1 eV, two C1s peaks are observed for g-C₃N₄ and MoO₂/g-C₃N₄ catalysts except MoO₂/g-C₃N₄-600. The peak at 284.8 eV ascribes to sp² C-C bonds of diffused oil as standard binding energy. The peak at 288.1 eV corresponds to N–C = N bonds in the tri-azine rings of g-C₃N₄ [43]. MoO₂/g-C₃N₄-600 sample (pure MoO₂) has no peaks at 288.1 eV, which reveals no existence of g-C₃N₄. C1s peaks at 288.1 eV for MoO₂/g-C₃N₄ composites shift to high binding energies compared with that of pure g-C₃N₄, suggesting strong interaction between the tri-azine rings and MoO₂. In Fig. 4b, N1s spectrum of pure g-C₃N₄ can be deconvoluted into three peaks located at 398.6 eV, 399.6 eV and 401.1 eV (Fig. S5), which are equivalent to pyridinic-N species, N atoms trigonal-bonding with sp² or sp³ carbon atoms, terminal amino-groups (–NH₂), respectively [44]. The main N1s peak at 398.6 eV for MoO₂/g-C₃N₄ composites shift to high binding energies compared with that of pure g-C₃N₄, which also means the strong synergetic effect between g-C₃N₄ and MoO₂. The peak at about 397 eV for MoO₂/g-C₃N₄ composites suggests the formation of Mo–N bond and the peak at around 395.5 eV belongs to Mo3p_{3/2} (Fig. S5) [45]. O1s spectra are displayed in Fig. 4c. MoO₂/g-C₃N₄-600 sample (pure MoO₂) shows a strong O1s peak at 530.7 eV which can be assigned to the O^{2–} in MoO₂. The O1s peaks for MoO₂/g-C₃N₄ composites locate at about 530.1 eV and shift to low binding energy compared with that of pure MoO₂, implying that MoO₂ interacts with g-C₃N₄. Mo3d peaks are shown in Fig. 4d. The binding energies of Mo⁴⁺ (3d_{5/2}, 3d_{3/2}) lie at around 229.7 and 232.9 eV, the binding energies of Mo⁶⁺ (3d_{5/2}, 3d_{3/2}) lie at 232.6 and 235.9 eV (Fig. S5) [29,46]. Partial surface Mo⁴⁺ chemical state of MoO₂ is oxidized to Mo⁵⁺ and Mo⁶⁺ due to the absorption of oxygen and hydroxyl groups. Compared with Mo3d binding energies of pure MoO₂, all the Mo3d peaks of MoO₂/g-C₃N₄ composites shift to low binding energies, and the amounts of Mo⁴⁺ species are also enhanced, giving clear evidences that electron transfer occurs from g-C₃N₄ to MoO₂.

As obtained above, comparing MoO₂/g-C₃N₄ composites with pure g-C₃N₄, C1s and N1s binding energies increase, while O1s and Mo3d binding energies decrease. This result clearly indicates the transference of electron from g-C₃N₄ nanosheets to well-dispersed MoO₂ nanoparticles, which will benefit the formation of heterojunction structure by combining MoO₂ with g-C₃N₄.

Fig. 5a shows the results of UV–vis diffuse reflectance spectra. Pure g-C₃N₄ exhibits a sharp absorption edge at 470 nm identical to 2.64 eV. MoO₂/g-C₃N₄ heterojunction composites present obvious red-shifts of the absorption edges due to the presence of metallic MoO₂. The background absorption for MoO₂/g-C₃N₄ composites is stronger than that for pure g-C₃N₄, which can be explained by the fact that the colors change from yellow to dark grey. Band gap energies of the as-synthesized composites are illustrated in Fig. 5b. Using the following equation, E_g of a semiconductor can be calculated:

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

Here E_g , α , h , ν and A represent band gap energy, absorption coefficient, Planck constant, photon frequency and a constant, respectively. n is 1 for direct gap semiconductor and n is 4 for indirect gap semiconductor. According to the plot of $\ln(\alpha h\nu) \sim \ln(h\nu - E_g)$ for g-C₃N₄ in this work, $n/2$ can be calculated from the slop to be 2 ($n = 4$), gives the evidence that g-C₃N₄ presents as an indirect band gap. This result is very consistent

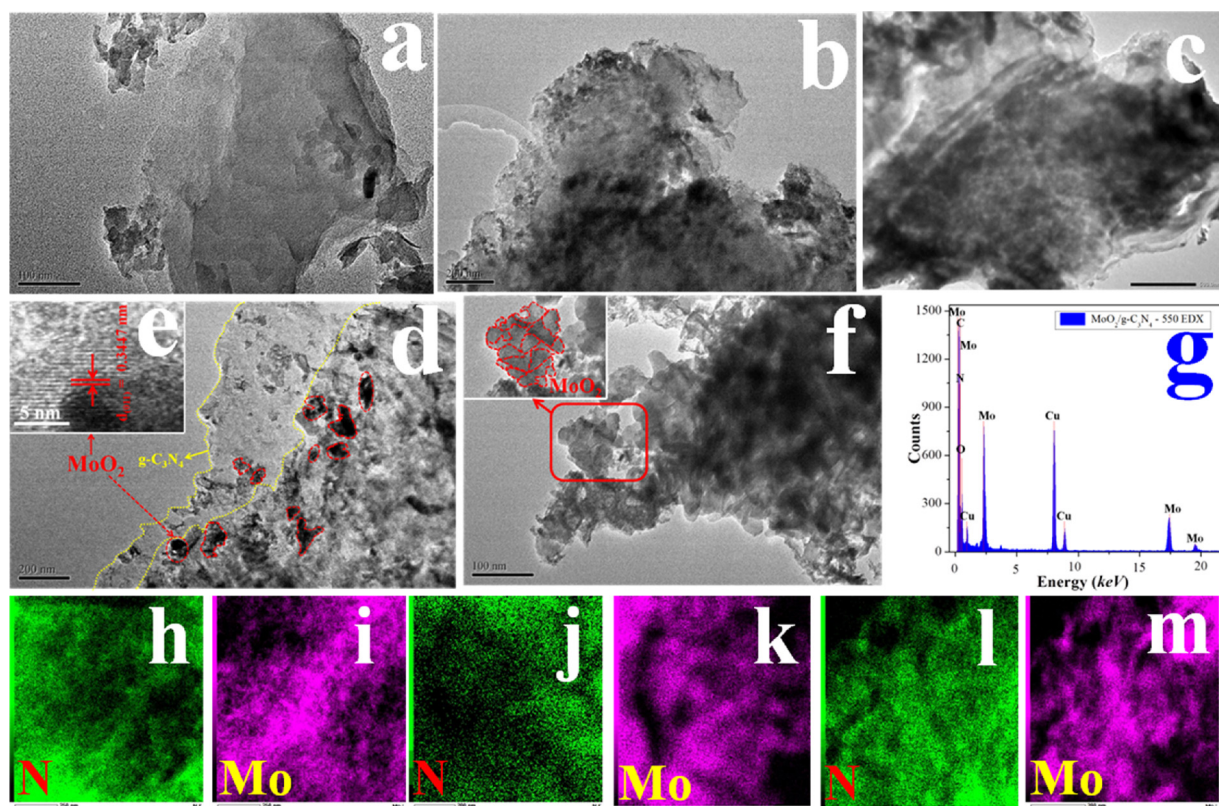
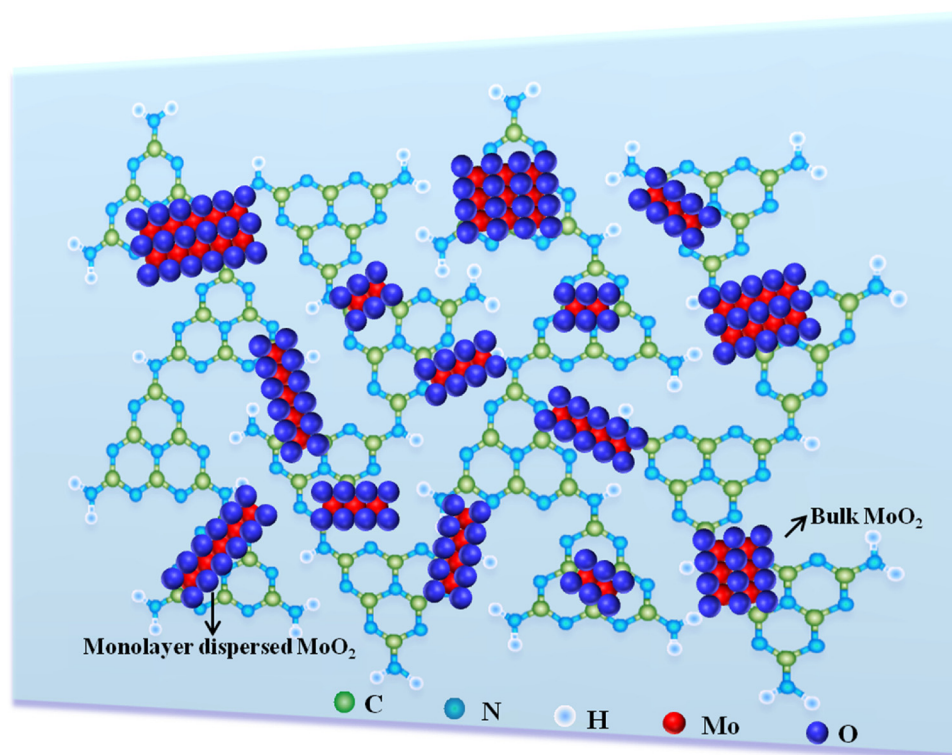


Fig. 3. (a) TEM image of pure g-C₃N₄ (b) TEM image of MoO₂/g-C₃N₄-450 (c) TEM image of MoO₂/g-C₃N₄-500 (d) TEM image of MoO₂/g-C₃N₄-550 (e) HRTEM image of MoO₂/g-C₃N₄-550 (f) TEM image of MoO₂/g-C₃N₄-600 (g) EDX spectrum of MoO₂/g-C₃N₄-550 (h,i) elemental mapping images of MoO₂/g-C₃N₄-450. (j,k) elemental mapping images of MoO₂/g-C₃N₄-500 (l,m) elemental mapping images of MoO₂/g-C₃N₄-550.



Scheme 3. Monolayer-dispersed MoO₂ and bulk MoO₂ on g-C₃N₄ nanosheet.

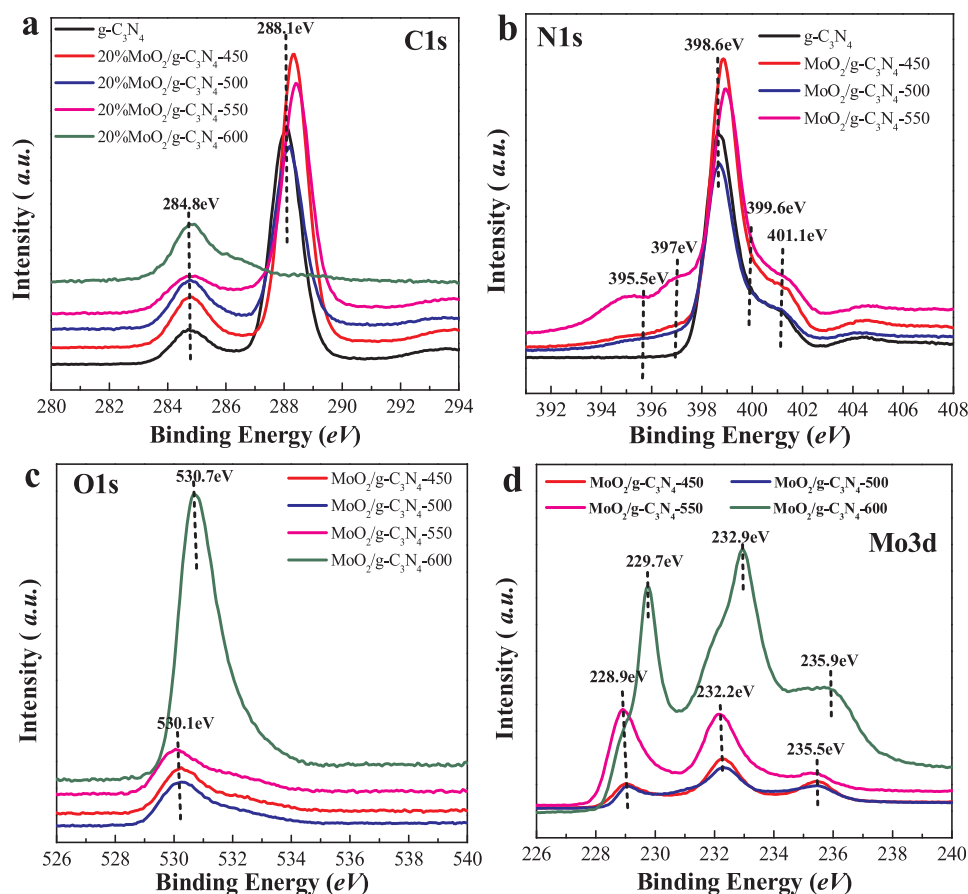


Fig. 4. XPS spectra of $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalysts (a) C1s, (b) N1s, (c) O1s, (d) Mo3d.

with the reported results according to UV–vis experiments [47] and DFT calculations [48]. Therefore in Fig. 5b, E_g of $\text{g-C}_3\text{N}_4$ is calculated to be 2.64 eV from a plot of $(ah\nu)^{1/2} \sim h\nu$, which is very close to the reported 2.67 eV [47]. The most interesting result is that the introducing of MoO_2 into $\text{g-C}_3\text{N}_4$ brings about a significant decrease in the band gap to 1.0–1.2 eV for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites, which clearly suggests the formation of heterojunction between metallic MoO_2 and semiconducting $\text{g-C}_3\text{N}_4$.

The Photoluminescence spectra of pure $\text{g-C}_3\text{N}_4$ and $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites are shown in Fig. 6. Pure $\text{g-C}_3\text{N}_4$ exhibits strong PL intensity at about 470 nm, which means a prompt recombination of electrons in CB and holes in VB. The PL result is in good accordance with the band

gap (2.64 eV) obtained from UV–vis spectra. With an increase in MoO_2 content for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites the PL emission intensity at 470 nm decreases sharply. $\text{MoO}_2/\text{g-C}_3\text{N}_4-600$ (pure MoO_2) shows no PL emission. The fact that the fluorescence of $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composite is obviously quenched verifies the existence of electron transfer from semiconducting $\text{g-C}_3\text{N}_4$ to metallic MoO_2 particles.

3.2. Evaluation of oxidative desulfurization activities

ODS activities of the as-synthesized $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalysts were examined via the oxidation of DBT using TBHP as the oxidant. The ODS experiments excluded the internal and external diffusion of the catalysts

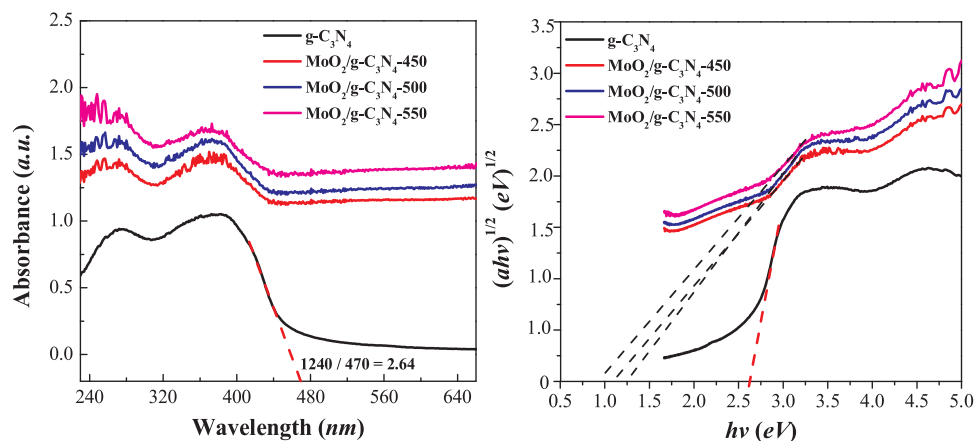


Fig. 5. (a) UV–vis diffuse reflection spectra of pure $\text{g-C}_3\text{N}_4$ and $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites (b) Plots of the $(ah\nu)^{1/2}$ vs. photon energy for pure $\text{g-C}_3\text{N}_4$ and $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites.

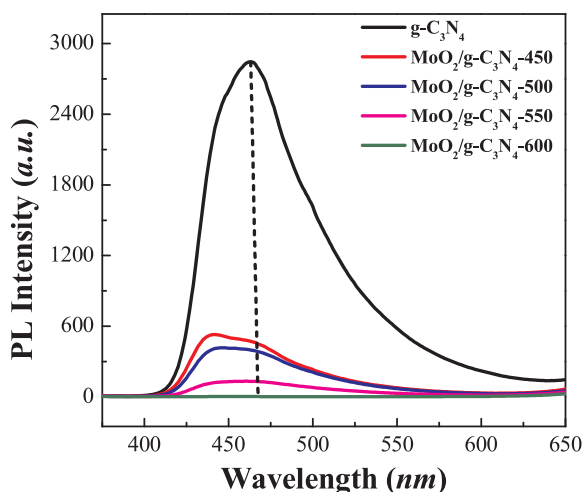


Fig. 6. Photoluminescence spectra of pure $\text{g-C}_3\text{N}_4$ and $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites.

by reducing the particles size (grinded to > 200 mesh) and increasing the reaction stirring speed. Fig. 7 shows the ODS results over the catalysts. The oxidation of DBT will not occur without catalyst or oxidant. With increasing MoO_2 contents in $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites, the ODS activities increase. It is apparent that $\text{MoO}_2/\text{g-C}_3\text{N}_4$ -550 catalyst exhibits excellent desulfurization performance which can successfully eliminate sulfur content to 0 ppm after 60 min's reaction. This result would be attributed to higher Mo loadings and more active sites for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ -550 catalyst. Therefore, to compare the intrinsic activity for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites, TON value is defined and calculated according to the formula of $\text{TON} = n/m$ (n is the mole of reacted DBT per gram catalyst, m is the mole of surface MoO_2 per gram catalyst). In the monoclinic MoO_2 ($P21/c$) crystal structure, each MoO_2 molecule occupies a volume of 32.9 \AA^3 , equivalent to an effective area of 10.2 \AA^2 . Therefore, the mole of surface MoO_2 can be calculated from the surface area of the $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalysts, assuming that the surfaces of the catalysts are completely covered by MoO_2 molecules. With increasing calcination temperatures and MoO_2 loadings, the TON values for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites decrease. $\text{MoO}_2/\text{g-C}_3\text{N}_4$ -450 sample shows the highest TON values, suggesting that the synergetic effect between MoO_2 and $\text{g-C}_3\text{N}_4$ with low Mo loading favors the ODS activity. As obtained by TEM results, MoO_2 presents the highest dispersion on $\text{g-C}_3\text{N}_4$ for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ -450 sample, implying that well-dispersed MoO_2 on $\text{g-C}_3\text{N}_4$ displays higher intrinsic ODS activity than bulk MoO_2 on $\text{g-C}_3\text{N}_4$. Therefore, the more effective electron transfer from $\text{g-C}_3\text{N}_4$ to well-dispersed MoO_2 offers the guarantee of higher electron density on

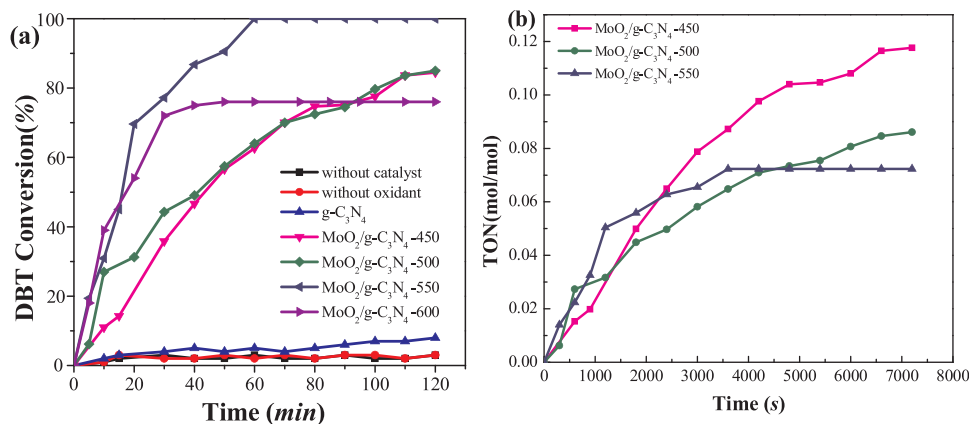


Fig. 7. (a) ODS activities over $\text{g-C}_3\text{N}_4$ and $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalysts. (b) Calculated TON values for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalysts. Reaction conditions: 10 g simulated diesel oil, 0.05 g catalyst, 353 K, O/S = 3:1.

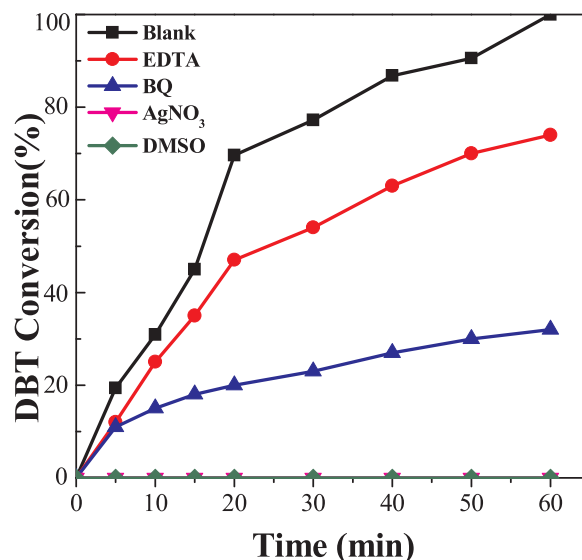


Fig. 8. ODS activities over $\text{MoO}_2/\text{g-C}_3\text{N}_4$ -550 catalyst with different scavengers. Reaction conditions: 60 min, 10 g simulated diesel oil, 0.05 g catalyst, 353 K, O/S = 3:1.

Mo active sites, which makes it possible to achieve higher intrinsic ODS activity.

In order to elucidate ODS reaction mechanism and the main reactive species, dimethyl sulfoxide (DMSO), ethylene diamine tetraacetic acid (EDTA) and p-benzoquinone (BQ) were used respectively as the scavengers for hydroxyl radicals ($\cdot\text{OH}$), holes (h^+) and superoxide radicals ($\cdot\text{O}_2^-$) [42,49]. Further, AgNO_3 aqueous solution is used as the scavengers for electrons (e^-). The results are shown in Fig. 8. All scavengers were added with excessive quantities (0.1 mmol, about 3 equivalent amounts of DBT). Compared with the blank scavenger-free experiment, the oxidation rate of DBT is inhibited slightly (15%) by the addition of EDTA, implying that holes (h^+) present as less important reactive species during ODS reaction. The addition of BQ severely inhibited the oxidation rate of DBT (62%), indicating $\cdot\text{O}_2^-$ radicals present as an important reactive species during ODS reaction. It is noteworthy that the addition of AgNO_3 aqueous solution and DMSO shows absolute inhibition effect on ODS reaction, which suggests that electrons (e^-) and hydroxyl radicals present as the most important reactive species during ODS reaction. The possibilities of AgNO_3 aqueous solution reacting with the oxidant TBHP are eliminated by the blank DBT-free experiments (There is no Ag precipitate observed or DMSO remains itself according to GC analysis). Thus, the $\cdot\text{OH}$ hydroxyl radicals and e^- electrons are proved to be the major active species for

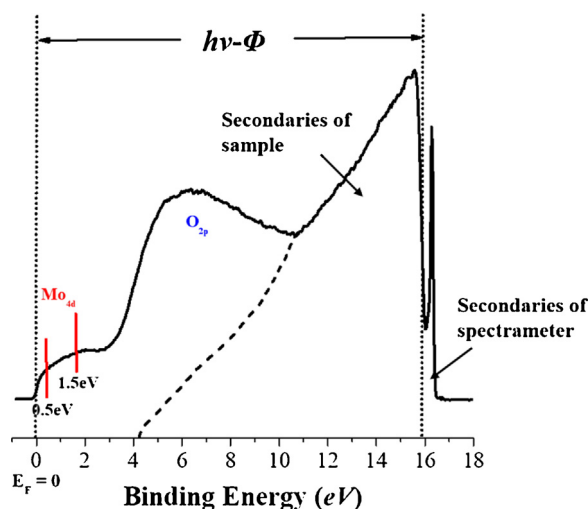


Fig. 9. UPS He I photoemission spectrum ($h\nu = 21.2$ eV) of MoO_2 .

ODS reaction on $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalyst.

3.3. Electronic structure of $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites

The electronic structure of pure MoO_2 is determined by UPS He I ($h\nu = 21.2$ eV) photoemission spectra (Fig. 9). In the spectra at low binding energy (0.5 and 1.5 eV) two peaks are found to be assigned to Mo_{4d} states, which are incorporated into a broad band ascribed to O_{2p} states. O_{2p} band successively incorporates into the peak attributed to secondary electron emission. d band at higher binding energy of 1.5 eV is appointed to $d_{//}$ band, and d band at lower binding energy of 0.5 eV is owing to π^* band as discussed in Scheme 2a. A significant decline in density of states at the Fermi level is observed in Fig. 9, suggesting that MoO_2 remains metallic character. The work function (Φ) of MoO_2 , defined to be the energy difference between the Fermi level and the vacuum level, is calculated by subtracting the incident He I photon energy from the energy extent of UPS spectrum when secondary electron emission of the sample is terminated ($21.2 - 15.9 = 5.3$ eV). Therefore, the Fermi level of MoO_2 relative to the vacuum level is -5.3 eV. The two Mo_{4d} peaks of MoO_2 just below Fermi level at ~ 0.5 and ~ 1.5 eV are also reported by other researchers [50,51].

As MoO_2 is expected for a metallic compound, DFT calculations are further performed to determine the electronic band structure and the wave functions. As shown in Fig. 10 a distinct metallic band structure is confirmed for the monoclinic MoO_2 (P21/c). The strong Mo-Mo dimerization discussed in Introduction results in the metallic behavior. The electronic density of states for MoO_2 are shown in Fig. 11. The

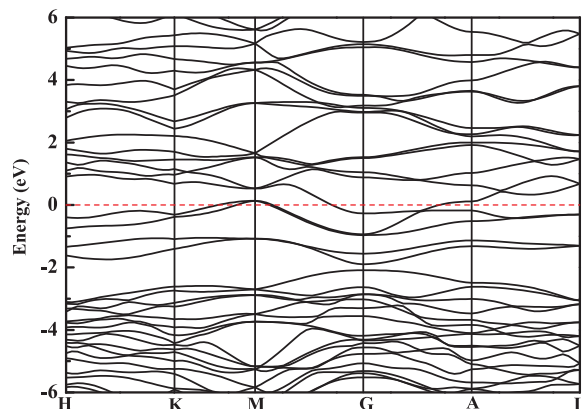


Fig. 10. Electronic band structure along the high-symmetry points for MoO_2 . The dashed line denotes the Fermi energy.

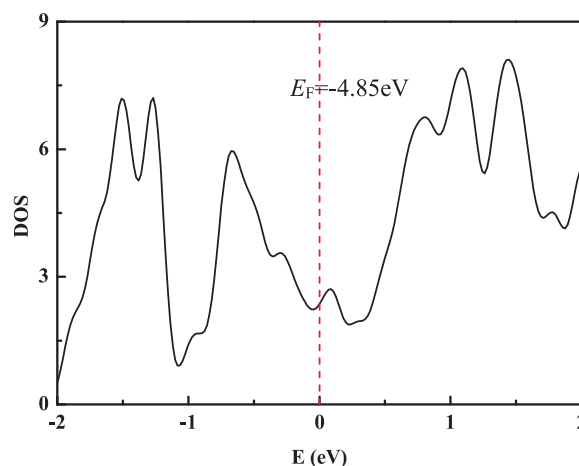


Fig. 11. Total electronic density of states for MoO_2 . The dashed line denotes the Fermi energy.

electronic structure close to the E_F is mainly contributed by Mo_{4d} character, which comprises two peaks at ~ 0.5 and ~ 1.5 eV below the Fermi energy ($E_F = -4.85$ eV). These results fit well with our UPS results and other reported theoretical DFT calculation results. [50,51].

To elucidate the nature of enhanced catalytic activity on $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composite, the VB and CB potentials of $\text{g-C}_3\text{N}_4$ vs SHE were calculated using the following formula:

$$E_{CB} = X - E^c - 1/2E_g$$

$$E_{VB} = E_{CB} + E_g$$

X is the electronegativity of $\text{g-C}_3\text{N}_4$ (4.73 eV) [52]. E^c is the energy of standard hydrogen electrode relevant to vacuum level ($E^c = 4.5$ eV). E_g is the band gap energy of $\text{g-C}_3\text{N}_4$ (2.64 eV). From the calculation, the E_{CB} of $\text{g-C}_3\text{N}_4$ is about -1.10 vs. SHE, and the E_{VB} of $\text{g-C}_3\text{N}_4$ is estimated to be 1.54 vs. SHE. Fig. 12 shows the electronic structure of $\text{MoO}_2/\text{g-C}_3\text{N}_4$ metal-semiconductor heterojunction. As obtained by UPS results, the Fermi level of MoO_2 is -5.3 eV, then the Fermi level vs. SHE is calculated to be $-(-5.3) - 4.5 = 0.8$. The excited thermoelectrons in the conduction band (carbon p_z orbitals containing free electrons) of $\text{g-C}_3\text{N}_4$ are easily transferred to the LUMO of Mo_{4d} band (unfilled π^* band, 0.5 eV below the Fermi level) of MoO_2 , a Schottky junction is then formed. The electron transfer inhibits the recombination of electrons in CB and holes in VB for $\text{g-C}_3\text{N}_4$, which leads to fluorescence quenching in PL spectra (Fig. 6). The electron transfer also results in high electron density on Mo (IV) active sites which may play an important role in ODS mechanism.

3.4. ODS mechanism on $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composites

We also make some meaningful attempt to understand the ODS mechanism on MoO_2 composites. Based on Mashio's research [53] and Kropp's research [54], we proposed the possible ODS mechanisms of DBT on MoO_2 with TBHP. Mashio et al. supposed that the five-member ring is formed through the coordination of *tert*-butyl hydroperoxide to Mo-O. Kropp et al. suggested that surface silanol groups of silica performed as the catalytic active sites to form a five-member ring with TBHP through hydrogen bonding.

Consequently, on the basis of the electronic structure of $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composite and the radical scavenger experiments, the most probable ODS mechanism is bring forward as shown in Scheme 4 when hydroxyl radicals and electrons act as the main reactive species. First, the chemisorption of TBHP on Mo-O active site leads to the formation of a coordinated five-member ring. Particularly, high electron density of Mo atom in $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composite facilitates the chemisorption of peroxy O atom with Mo atom. The electron scavengers AgNO_3

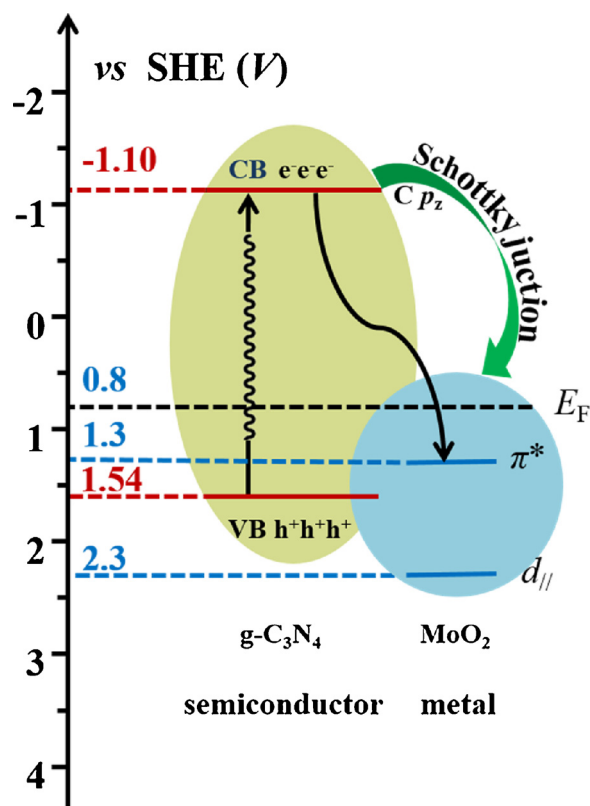


Fig. 12. The electronic structure of MoO₂/g-C₃N₄ metal-semiconductor heterojunction.

absolutely inhibit the ODS reaction, giving the evidence that electron transfer is the most important step. In step 1, attributing to high electron density on Mo atom (some electrons transferred from g-C₃N₄), electron transfer will easily occur from Mo to neighboring O2 atom. High electron density on O2 atom brings about easier O–O bond cleavage, which leads to the formation of $\cdot\text{OH}$ radicals. In step 2, the formed $\cdot\text{OH}$ radicals show high oxidizability, the sulfur atom of DBT then nucleophilic attacks the specific O1 atom leading to the formation

of sulfoxide. Therefore, step 1 including electron transfer and O–O bond cleavage acts as the rate-determining step.

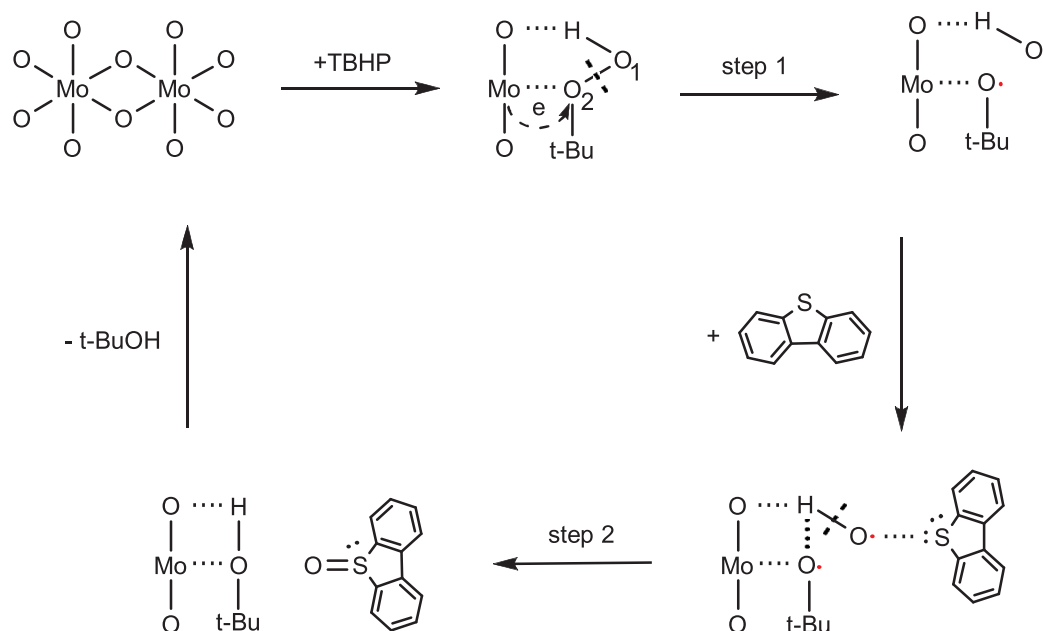
BQ shows an inhibition effect of 61% on the ODS reaction, implying that $\cdot\text{O}_2^-$ may also present as a reactive species. So another possible ODS mechanism is shown in Scheme 5. In step 1 O–H bond cleavage is suggested to happen instead of O–O bond cleavage. Tert butyl cation with relative stability may also be formed, then superoxide radicals is produced in this step. $\cdot\text{O}_2^-$ presents high oxidizability which can oxidize the sulfur atom in DBT easily.

To further investigate the feasibility of the above two reaction pathways, the energy barriers were calculated by the CI-NEB method. To simplify the calculation, model molecule of hydrogen peroxide is used as a substitute for TBHP oxidant. As shown in Fig. 13, the ODS reaction on MoO₂ experiences the five-member ring transition state. When O–O bond cleavage leads to the formation of hydroxyl radicals ($\cdot\text{OH}$), the activation energy of the reaction is only required to be 0.24 eV and the reaction is exothermic. When the cleavage of H–O bond to form $\cdot\text{OOH}$ radicals is required, the activation energy of the reaction is 2.68 eV and the reaction is endothermic. Thus, hydroxyl radical is suggested to be more easily formed on MoO₂ in ODS reaction.

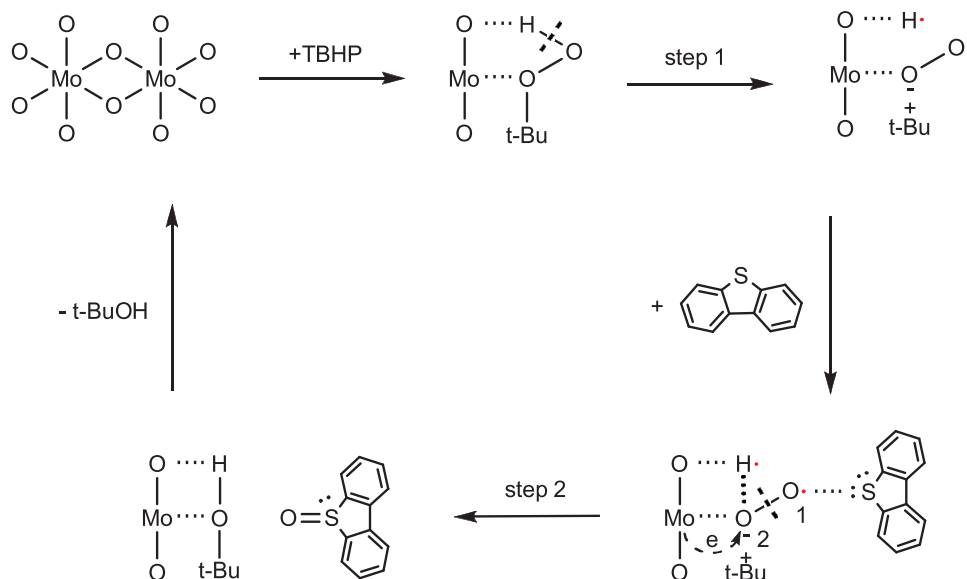
4. Conclusions

In summary, we present here MoO₂/g-C₃N₄ as a metal-semiconductor heterojunction. The nature of synergic effect between MoO₂ and g-C₃N₄ is particularly elucidated.

- (1) MoO₂/g-C₃N₄ composites with different MoO₂ contents (19–50 wt %) have been successfully synthesized by a facile calcination method.
- (2) XPS results clearly indicate that electron transfer from g-C₃N₄ to MoO₂ occurs for MoO₂/g-C₃N₄ heterojunction composite.
- (3) Through UV–vis results, the introducing of MoO₂ into g-C₃N₄ decreases the band gap from 2.64 eV of g-C₃N₄ to 1.0–1.2 eV of MoO₂/g-C₃N₄, which indicates the metallic character of MoO₂.
- (4) According to UPS results, a significant decline in density of states at the Fermi level ($E_F = -5.3$ eV) is observed for pure MoO₂, suggesting that MoO₂ presents metallic character.
- (5) The electron transfer from the valence band of g-C₃N₄ to unfilled Mo_{4d} band of MoO₂ prevents the recombination of electrons and



Scheme 4. The most probable ODS mechanism of t-BuO₂H → t-BuO \cdot + $\cdot\text{OH}$ on MoO₂/g-C₃N₄ catalyst.



Scheme 5. Another possible ODS mechanism of $t\text{-Bu}_2\text{O}_2\text{H} \rightarrow t\text{-Bu}^+ + \text{O}_2^- + \cdot\text{H}$ on $\text{MoO}_2/\text{g-C}_3\text{N}_4$ catalyst.

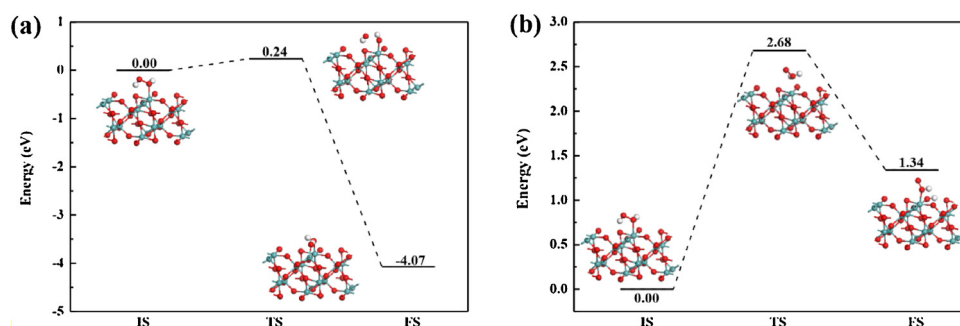


Fig. 13. Reaction pathway of dissociation of H_2O_2 on MoO_2 (011): (a) $\text{H}_2\text{O}_2 \rightarrow \text{HO}\cdot + \cdot\text{OH}$ (b) $\text{H}_2\text{O}_2 \rightarrow \text{HOO}\cdot + \cdot\text{H}$.

holes, which leads to fluorescence quenching in PL spectra. The electron transfer also results in high electron density on Mo atom and a Schottky junction is then formed.

- (6) Hydroxyl radicals and e^- electrons are proved to be the major reactive species for ODS reaction on $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composite.
- (7) Well-dispersed MoO_2 on $\text{g-C}_3\text{N}_4$ displays higher intrinsic ODS activity than bulk MoO_2 on $\text{g-C}_3\text{N}_4$ due to the higher electron density of Mo active sites.
- (8) High electron density of Mo atom for $\text{MoO}_2/\text{g-C}_3\text{N}_4$ composite facilitates O–O bond cleavage, which is responsible for the rate-determining step in ODS reaction.
- (9) Theoretical calculations indicate that MoO_2 presents metallic band structure and hydroxyl radical is easily formed on MoO_2 in ODS reaction.

The present results open new vistas for redox reaction using metal-semiconductor structures as the functional catalyst.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.07.037>.

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